Immobilization of nanofibrous metal oxides on microfibers: A macrostructured catalyst system functionalized with nanoscale fibrous metal oxides†

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Nanofibrous LaMnO$_3$ can be immobilized on macrostructured materials using carbon nanofibers as templates; their application as macro-nanostructured catalysts are also presented.

Nanoscale materials are expected to be potential catalysts in future chemical industries. The design of materials at a nano-level brings about attractive catalytic properties due to the quantum effect, the control of the reaction field, or the increase in the number of active sites. In fact, the efficiency and selectivity of reactions, and the recovery and recyclability of catalytic materials, have been improved by using appropriate nanoscale materials as catalysts.[1]
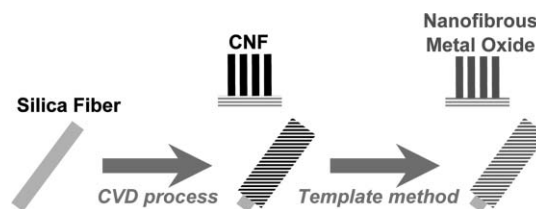
To achieve high efficiency in the utilization of energy, and also high reaction yield in practical applications, not only is the nanoscale form of the catalyst a key factor, but also its macroscale form. Regardless of the synthetic method, most prepared nanoscale materials are obtained in a powdered form. Utilization of powders in conventional catalytic reactions is problematic because powder form catalysts are at a disadvantage in pressure drop, mass/heat transfer, contacting efficiency and separation processes.[2] Therefore, the design of a catalyst's form at a macroscale is indispensable to avoid these problems. From these viewpoints, macrostructured materials have drawn attention as catalytic supporting materials.[2] Monolithic, fibrous and foaming materials are typical macrostructured materials. However, their chemical inertness or low surface area make it difficult to utilize "bare" macrostructured materials for catalytic reactions. Thus, their surface must be functionalized. If nanoscale materials with attractive catalytic properties can be immobilized on macrostructured materials, they must be effective structured catalysts designed at both nano- and macroscales. Up to now, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been immobilized on cordierite monolith,[3] Ni foam[4] and graphite felt.[5] This has been achieved through chemical vapour deposition (CVD) over macrostructured materials. CNFs immobilized on graphite felt were successfully used as a support for a high loaded Ir catalyst in

the decomposition of hydrazine.[5a] In addition, CNFs immobilized on graphite felt showed stable performance to the oxidative dehydrogenation of ethyl benzene.[5c] However, direct utilization of CNTs/CNFs for catalytic reaction systems have been regrettably limited because carbonaceous materials are primarily inert for most chemical reactions and are easily decomposed into gaseous compounds under oxidative or reductive atmospheres at high temperature.[6]

In contrast, metal oxides are effective catalysts for many heterogeneous catalytic reactions, and most of them are stable under severe conditions. Here, we demonstrate the immobilization of nanofibrous metal oxides on macrostructured materials by combining the CVD process and template method. The template method is a typical fabrication method for metal oxide nanotubes/nanofibers.[7] Metal oxide nanotubes/nanofibers are synthesized by the coating of templates with a metal oxide, followed by removal of the templates. We have already reported the synthesis of various oxide nanotubes/nanofibers using CNFs as templates.[8] As mentioned above, one of the notable features of CNFs is their formation on various substrates through a CVD process. Using this feature of CNFs, we attempted the immobilization of nanofibrous metal oxide on macrostructured materials.

Fig. 1 shows a schematic representation of the procedure used. In this study, silica fibers were used as macrostructured materials. Firstly, a small quantity of Ni particles (which catalyze CNF growth) were attached onto the silica fibers. The contact of methane with silica fiber-supported Ni (*i.e.*, a CVD process) brought about the growth of CNFs on silica fibers. As a result, CNFs were immobilized on the silica fibers. Immobilized CNFs can be used as templates for metal oxide nanotube/nanofiber synthesis. Eventually, these procedures will produce silica fiber-immobilized metal oxide nanotubes/nanofibers.

Silica fibers (Tosoh Corporation) were immersed into an acetone solution of Ni(NO$_3$)$_2$·6H$_2$O (0.3 M). The solution was placed in a suction filtration unit (Büchner funnel with filter

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Fig. 1 The fabrication process of nanofibrous metal oxides immobilized on microfibers.

paper). To remove the excess solution, silica fibers soaked with the solution were pressed under filtration. After this procedure, a small amount of the acetone solution of $Ni(NO_3)_2 \cdot 6H_2O$ remained on the surface of the silica fibers. By calcinating the resulting samples in air at 573 K for 30 min, silica fiber-supported NiO (ca. 1 wt% as NiO) was obtained. 0.2 g of silica fiber-supported NiO was placed in a quartz reactor. The CVD process was carried out by the contact of a stream of methane (P_{CH_4} = 101 kPa, flow rate = 20 ml min^{-1}) at 823 K for 2 h. Immobilization of nanofibrous $LaMnO_3$ on the silica fibers was carried out as follows: An acetone solution of $La(NO_3)_3 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ was prepared (0.3 M as total metals, La/Mn = 1 : 1). After the silica fiber-immobilized CNFs had been immersed in the resulting solution, the sample was placed in a suction filtration unit (Büchner funnel with filter paper). To remove the excess solution that had not penetrated into the immobilized CNFs, the sample was pressed under filtration and dried at 573 K for 30 min. In the drying process, the metal nitrates were adsorbed and decomposed on the surface of the CNFs. This coating process was repeated four times. Finally, the CNF templates were removed by calcination in air at 923 K.

The typical morphology of the initial silica fibers was straight, and the diameter was ca. 5 μm (Fig. 2(a)). After the CVD process, the weight of samples increased two-fold. The diameter of the resulting samples was larger than that of the original silica fibers (Fig. 2(b)). In addition, the CVD process resulted in a drastic color change of the samples; the initially white silica fibers turned black (insets of Fig. 2(a) and Fig. 2(b)). These results strongly suggest that a large quantity of CNFs grow uniformly on the silica fibers. A high magnification SEM image shows that CNFs of ca. 50–100 nm diameter are immobilized and that their shapes are curved (Fig. 2(c)). Using CNFs grown on silica fibers as templates, we demonstrated the immobilization of $LaMnO_3$ on silica fibers. A typical SEM image of prepared silica fiber-immobilized $LaMnO_3$ is shown in Fig. 2(d). It is obvious that the diameter of the formed materials is much larger than that of the original silica fibers. This increase in diameter clearly suggests that the silica fibers are uniformly coated with a thick layer of $LaMnO_3$. The weight percent of $LaMnO_3$, estimated by the changes in weight, was ca. 30 wt%. In a high magnification SEM image, the net-like structure

of the immobilized $LaMnO_3$ is visible (Fig. 2(e)). All the $LaMnO_3$ formed on the silica fibers is of net-like structure. EDX analysis shows that the molar ratio of La/Mn is ca. 1 : 1. Elemental analysis indicates that no C, H or N are contained in the silica fiber-immobilized $LaMnO_3$. Thus, CNFs are completely removed by the calcination treatment.

As a control experiment, the coating of $LaMnO_3$ onto silica fibers without CNFs was performed. The resulting SEM image shows that no changes in diameter of the silica fibers occurred (Fig. 2(f)), suggesting that the immobilization of $LaMnO_3$ onto the silica fibers was due to the CNFs. In addition, nanofibrous $LaMnO_3$ could be immobilized onto another macrostructured material (SiC fibers), and another nanofibrous metal oxide (ZrO_2) could be immobilized onto silica fibers (Fig. S1†) through a similar process.

Cross-sectional TEM measurements are particularly useful for investigating coating layers. Therefore, TEM images of sections of silica fiber-immobilized CNFs and $LaMnO_3$ were measured. In the cross-sectional TEM images, the absence of some silica fibers inside the CNF or $LaMnO_3$ layers is due to the breakage of silica fibers through cutting by an ultramicrotome. A TEM image of sections of silica fiber-immobilized CNFs show that the CNF layer is 5–6 μm in thickness (Fig. 3(a)). CNFs grow densely within the inner coating but are distributed more thinly towards the outer edge. As the CNFs grow away from the silica fibers, the spaces where the CNFs can grow become larger. Eventually, the outer layer of CNFs become thin. In the case of $LaMnO_3$ layers, they are 3–6 μm in thickness, and the inner layer is dense while the outer layer is thin (Fig. 3(b)). That is to say, cross-sectional TEM images show that the shapes of $LaMnO_3$ layers are similar to those of CNF layers, implying that CNFs acted as templates. Fig. 3(c) and Fig. 3(d) show TEM images of the immobilized $LaMnO_3$ torn from silica fibers by ultrasonic treatment. Obviously, the shapes of the immobilized $LaMnO_3$ are nanofibrous. This corresponds to the results of SEM measurements (Fig. 2(e)). It seems that nanofibrous $LaMnO_3$ consist of $LaMnO_3$ crystallites of several-ten nanometers. TEM images suggest that the networks consist of nanofibrous $LaMnO_3$ thickly-covered silica fibers.

The bulk structure of the silica fiber-immobilized nanofibrous $LaMnO_3$ was identified from X-ray diffraction (XRD) patterns.
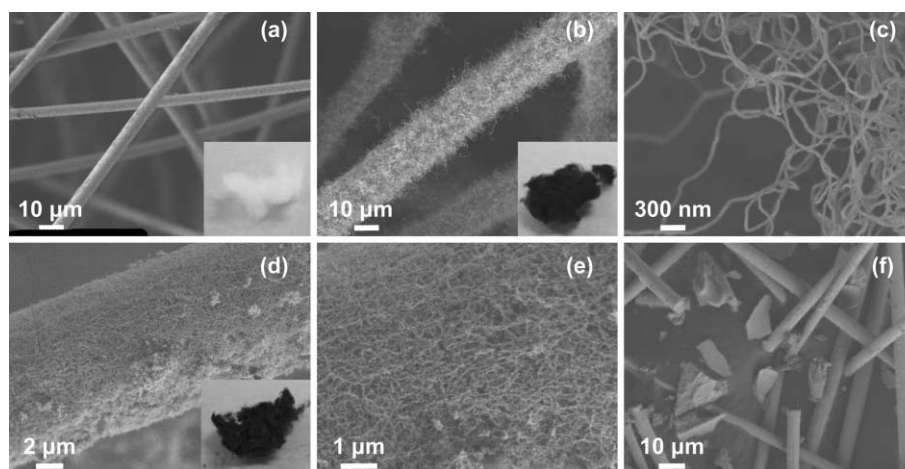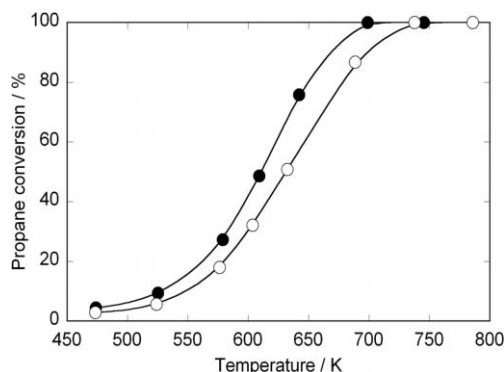

Fig. 2 SEM images of (a) silica fibers, (b/c) silica fiber-immobilized CNFs, (d/e) silica fiber-immobilized nanofibrous $LaMnO_3$ and (f) silica fiber–$LaMnO_3$ composites synthesized without CNFs. Insets show the micrographs of the obtained samples.
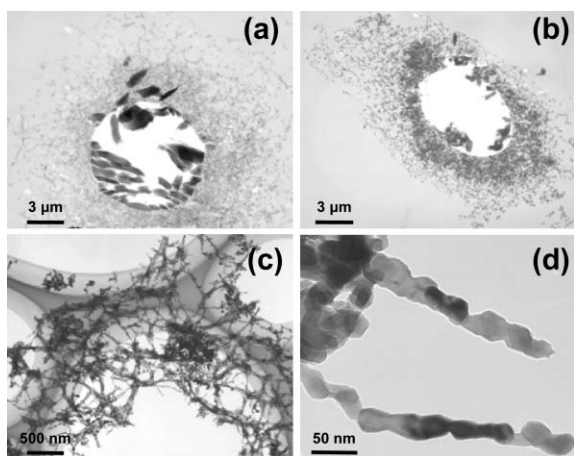
Fig. 3 TEM images of (a) cross-sections of silica fiber-immobilized CNFs, (b) cross-sections of silica fiber-immobilized nanofibrous LaMnO$_3$ and (c/d) immobilized nanofibrous LaMnO$_3$.

Fig. 4 Propane oxidation over silica fiber-immobilized nanofibrous LaMnO$_3$ (●) and LaMnO$_3$ powder catalysts (○).

The XRD patterns showed only diffraction lines attributable to the perovskite structure of LaMnO$_3$ (Fig. S2†). The average crystallite size of nanofibrous LaMnO$_3$, estimated using Scherrer's equation, was 23.5 nm. This crystallite size seems to correspond to the size of the crystallite observed in the TEM image (Fig. 3(d)). Specific surface areas were measured by nitrogen adsorption at 77 K. Samples were de-gassed under vacuum at 573 K for 3 h prior to the sorption measurements, and surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The specific surface area of the nanofibrous LaMnO$_3$, estimated by subtracting the surface areas of the silica fibers (1 m^2 g^{-1}) from that of the silica fiber-immobilized nanofibrous LaMnO$_3$, was 36 m^2 g^{-1}.

Next, we tested the catalytic performance of the prepared materials. Volatile organic compounds (VOCs) emitted by many industrial processes can cause a danger to human health. Catalytic combustion is one of the most promising processes for the removal of VOCs. La-based perovskite-type oxides are well known as effective combustion catalysts.[9] Therefore, the catalytic performance of silica fiber-immobilized nanofibrous LaMnO$_3$ was tested in the complete oxidation of propane, which was chosen as a model VOC. As reference catalysts, LaMnO$_3$ powder catalyst was prepared by the citrate method. The citrate method is a typical synthesis method for perovskite-type oxides with high surface areas.[9] XRD patterns of the LaMnO$_3$ powder showed only diffraction lines attributable to a perovskite structure (Fig. S2†). The crystallite size, estimated from XRD patterns, was 27.6 nm, and its specific surface area was 26 m^2 g^{-1}. It is noted that the surface area of nanofibrous LaMnO$_3$ is 1.4 times larger than that of LaMnO$_3$ powder prepared by the citrate method. Fig. 4 shows the propane conversion as a function of reaction temperature during propane oxidation over silica fiber-immobilized nanofibrous LaMnO$_3$ and LaMnO$_3$ powder catalysts. The weight of LaMnO$_3$ in both catalysts is same. The formation of only CO$_2$ and H$_2$O was observed, indicating the complete oxidation of propane. It can be seen that silica fiber-immobilized nanofibrous LaMnO$_3$ showed higher activity for propane oxidation than did the LaMnO$_3$ powder. The propane conversions were 27.3% for silica fiber-immobilized nanofibrous LaMnO$_3$ (579 K) and 18.0% for LaMnO$_3$ powder (576 K), indicating that the silica fiber-immobilized nanofibrous LaMnO$_3$ showed ca. 1.5 times higher activity than did the LaMnO$_3$ powder. It is considered that this difference in the catalytic activities is due to the differences in their surface areas. As mentioned above, the citrate method is a typical synthesis process for perovskite-type oxide nanoparticles with high surface areas (i.e., high catalytic activity). Therefore, the results in Fig. 4 strongly suggest that catalytically active nanofibrous LaMnO$_3$ catalysts, due to their high surface area, can be immobilized on silica fibers.

This work introduces an immobilization method for nanofibrous metal oxides. Nanofibrous LaMnO$_3$ immobilized on microfibrous silica is a structured material that is designed at both nano- and macroscales. This macro-nanostructured material showed high catalytic activity due to its high surface area.

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